



## Short communication

## Introduction of two lithiooxycarbonyl groups enhances cyclability of lithium batteries with organic cathode materials



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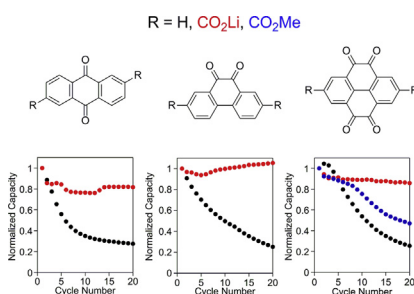
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## HIGHLIGHTS

- Organic cathode materials of low molecular weights suffer from low cyclability.
- We report a new approach to increase the cyclability of organic lithium batteries.
- *p*- and *o*-quinones having two  $\text{—CO}_2\text{Li}$  groups exhibited improved cyclability.
- $\text{—CO}_2\text{Li}$  groups do not strongly affect the redox potentials of quinones.
- The battery using pyrenetetraone having two  $\text{—CO}_2\text{Li}$  exhibited high performance.

## GRAPHICAL ABSTRACT



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## ABSTRACT

To increase the cyclability of lithium batteries using organic cathode materials of low molecular weights, two lithiooxycarbonyl ( $\text{—CO}_2\text{Li}$ ) groups was introduced to *p*- and *o*-quinones. The introduction of two  $\text{—CO}_2\text{Li}$  groups does not strongly affect the redox potentials of quinones. Lithium batteries using *p*- and *o*-quinones with two  $\text{—CO}_2\text{Li}$  groups as cathode materials exhibit excellent cyclability compared to their parent quinones. In particular, pyrene-4,5,9,10-tetraone having two lithiooxycarbonyl groups (LCPYT) exhibited high energy density, high cyclability, and fast charge ability. These results indicate that introduction of two lithiooxycarbonyl groups to quinones serves as a simple and effective way to decrease the solubility of various quinones in electrolyte solutions without significant decrease in the voltage.

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## 1. Introduction

High performance organic cathode materials for lithium-ion batteries [1–3] have received significant research interest because of sustainability [4], flexibility [5], and versatile molecular design. Many organic cathode materials [6] such as electrochemically active polymers [7], organosulfur compounds [8], quinones [9–20], other carbonyl compounds [21–28], nitroxides [29–32], and

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trioxotriangulene [33,34] have been developed so far. We have also studied organic cathode materials based on our background of organic electrochemistry [35–38], and have recently found that polymer-bound pyrenetetraone [39] serves as an excellent material from view-points of capacity, cyclability, and the charge–discharge rate.

Although some organic cathode materials exhibit higher capacity than inorganic materials such as  $\text{LiCoO}_2$ , organic cathode materials of low molecular weights generally suffer from high solubility in electrolyte solutions, which significantly reduces cyclability of batteries. To decrease the solubility, introduction of heavy atoms [33], or incorporation of an organic material to covalent polymers [29,39] is effective. In addition, study of quasi-solid-state Li-ion battery with monomeric organic materials has been reported [40,41]. However, these methods still need some improvements. Therefore, a simple approach to decrease the solubility of organic cathode materials is highly required.

In this regards, the use of interaction between a lithium ion and organic anions is very promising [12,13,15]. A drawback of the previously reported salt formation such as lithiooxy ( $-\text{OLi}$ ) groups would be a decrease of the discharge voltage due to the electron donating nature of the lithiooxy groups.

Here we show an alternative approach to this problem, i.e. decreasing the solubility of organic cathode molecules by the introduction of two lithiooxycarbonyl ( $-\text{CO}_2\text{Li}$ ) groups, which are expected to exhibit strong intermolecular interaction. One of the possible interactions is shown in Fig. 1a [42]. In addition, the

Hammett values ( $\sigma_p$  and  $\sigma_m$ ) for  $\text{COO}^-$  is 0.11 and 0.02, respectively, while those for  $\text{O}^-$  is  $-0.87$  and  $-0.47$ , respectively [43]. Therefore, introduction of  $-\text{CO}_2\text{Li}$  groups is not expected to strongly affect the redox potentials of the parent structure. Although the charge–discharge properties of  $\pi$ -conjugated compounds having two  $-\text{CO}_2\text{Li}$  groups are reported, they are used as organic anode materials utilizing the low redox potential of  $-\text{CO}_2\text{Li}$  groups [44–47]. Very recently, Poizot's and Tao and Chen's groups have reported the use of dilithium (2,5-dilithiooxy)terephthalate as a cathode material for lithium battery [48,49]. However, the generality of the method has not been indicated. In this study we revealed that the concept of increasing cyclability without affecting the voltage of the batteries by the introduction of two  $-\text{CO}_2\text{Li}$  groups is generally applicable to various quinones by computational and experimental studies. Herein we report the results of this study including the synthesis of *p*- and *o*-quinones having two  $-\text{CO}_2\text{Li}$  groups, their redox properties, and the charge–discharge properties of Li-ion batteries using them.

## 2. Experimental

### 2.1. Materials

We studied *p*- and *o*-quinone derivatives having two  $-\text{CO}_2\text{Li}$  groups (LC-quinones), i.e. 2,6-bis(lithiooxycarbonyl)-9,10-anthraquinone (LCAQ), 2,7-bis(lithiooxycarbonyl)-9,10-phenanthrenequinone (LCPQ), and 2,7-bis(lithiooxycarbonyl)pyrene-4,5,9,10-

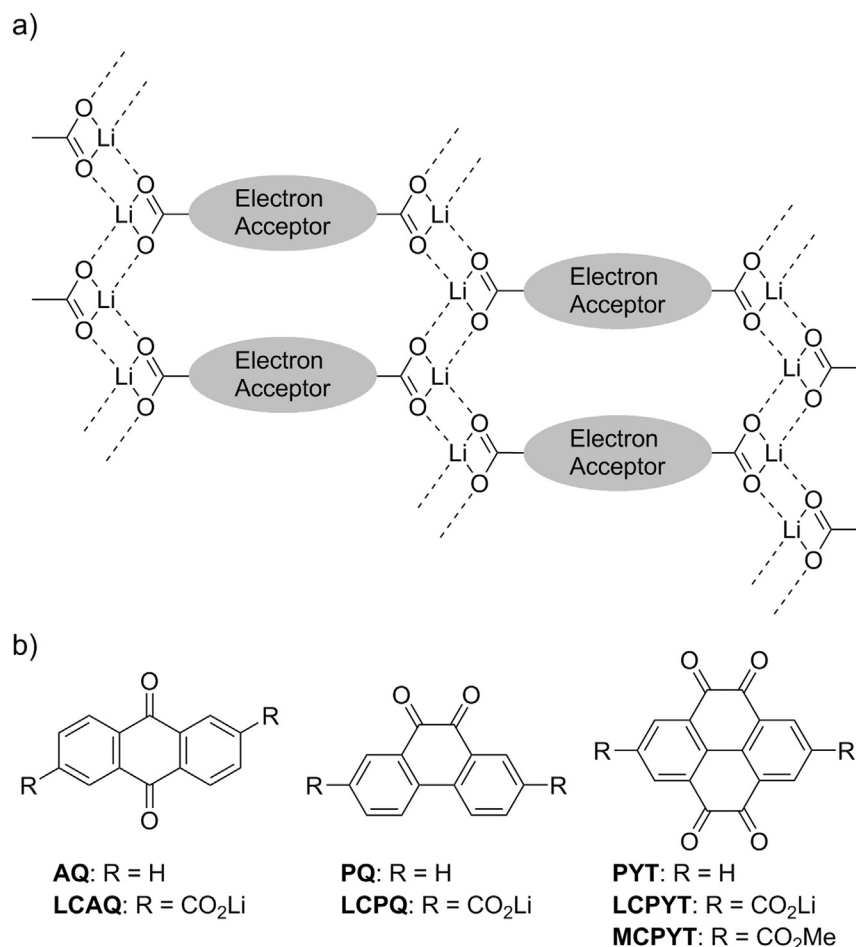


Fig. 1. a) Schematic drawing of the role of  $-\text{CO}_2\text{Li}$  groups, and b) structures of quinones and LC-quinones.

tetraone (LCPYT), whose theoretical capacities are 174, 174, and 296 mAh g<sup>-1</sup>, respectively (Fig. 1b). We also studied 2,7-bis(methoxycarbonyl)pyrene-4,5,9,10-tetraone (MCPYT), whose theoretical capacity is 283 mAh g<sup>-1</sup>, to examine the effect of the –CO<sub>2</sub>Li group on the cyclability. Scheme 1 shows synthetic procedures for LCAQ, LCPQ, LCPYT, and MCPYT. LCAQ was synthesized from 2,6-dibromo-9,10-anthraquinone (**1**). Cyanation of **1** and subsequent hydrolysis of the cyano groups gave the dicarboxylic acid **2** [50,51], which was neutralized by lithium hydroxide to give LCAQ. LCPQ was synthesized from 2,7-diiodo-9,10-phenanthrenequinone (**3a**) [52]. Protection of the *o*-quinone structure of **3a** with 1,2-ethanediol gave the protected diiodo-compound **4a**. Cyanation of **4a** and subsequent hydrolysis of the cyano groups gave the protected dicarboxylic acid **6a**. Deprotection of **6a** gave the dicarboxylic acid **7a**, which was neutralized by lithium hydroxide to give LCPQ. LCPYT was synthesized with the same procedure as LCPQ from 2,7-diiodopyrene-4,5,9,10-tetraone (**3b**) [52,53]. MCPYT was synthesized by methylation of **7b**. LCAQ, LCPQ, LCPYT, and MCPYT exhibited thermal stability at around 350 °C, which is an important property for safety of Li-ion batteries (Fig. S1).

## 2.2. DFT calculations

DFT calculations were performed with the Gaussian 09 program [54]. All geometry optimizations were carried out at the B3LYP level of density functional theory with the 6-31G(d) basis set.

## 2.3. Preparation of electrodes and cells

Battery performances of LC-quinones and parent quinones as cathode materials were examined using a lithium anode in charge–discharge cells. Cathodes were prepared by mixing AQ, LCAQ, PQ, LCPQ, PYT, LCPYT, or MCPYT with acetylene black (AB; Denki Kagaku Kogyo) and poly(tetrafluoroethylene) (PTFE; Daikin

Industries, Ltd.) as a binder (ratio: 1.5/4.0/1.0 wt %). These materials were mixed, and pressed on aluminum mesh. Hermetically sealed two-electrode cells were used for electrochemical experiments. The cathode (weight ca. 4.2 mg; 10 mm × 10 mm square) was separated from the lithium anode (The Honjo Chemical Corp.) by the polyethylene porous film (celgard) imbibed with 1 M LiPF<sub>6</sub>/propylene carbonate (LiPF<sub>6</sub>/PC) or an equimolar complex LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>/tetraglyme (LiTFSA/G4). The three layers were pressed between two current collectors, one in contact with the cathodic material and the other in contact with a lithium disk.

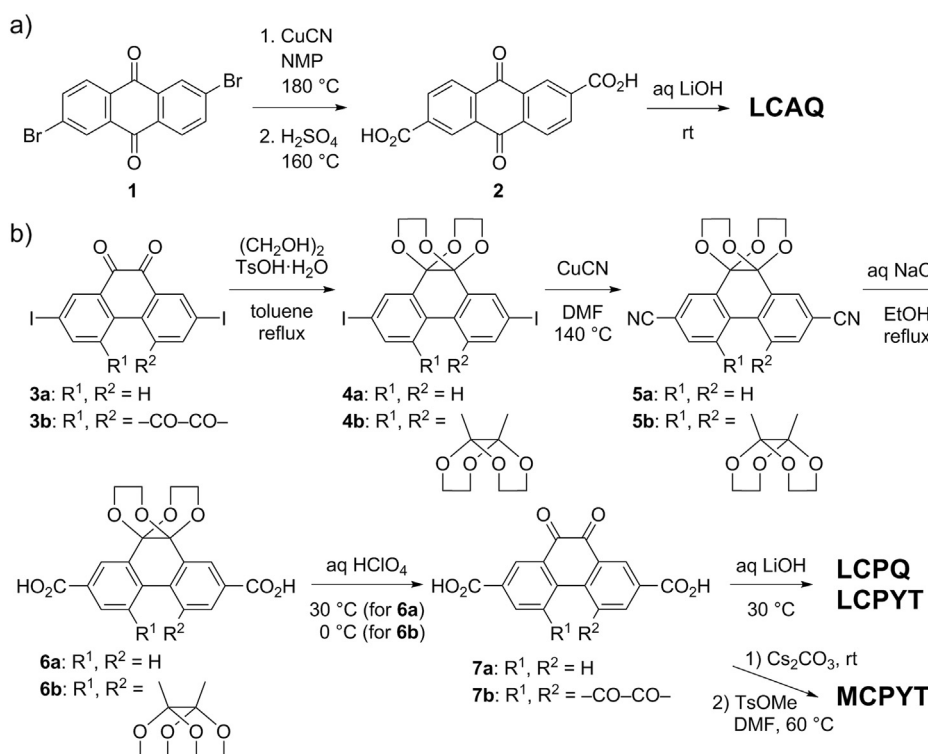
## 2.4. Electrochemical analyses

Cyclic voltammogram were measured on an HCH Instruments ALS Model 700d electrochemical analyzer. The measurements were carried out with a glassy carbon rod as a working electrode coupled with a Pt plate counter electrode and Ag/AgNO<sub>3</sub> electrode as a reference electrode in dimethyl sulfoxide (DMSO) containing 0.1 M LiBF<sub>4</sub> as the supporting electrolyte. Galvanostatic experiments were performed using BAS 700D and Solartron 1287. The electrode rate capability was examined at the 0.2 C rate. Experiments were performed at 25 °C for LiPF<sub>6</sub>/PC and 45 °C for LiTFSA/G4. The charge–discharge capacities were determined on the basis of the weight of LC-quinones or parent quinones in the cathode.

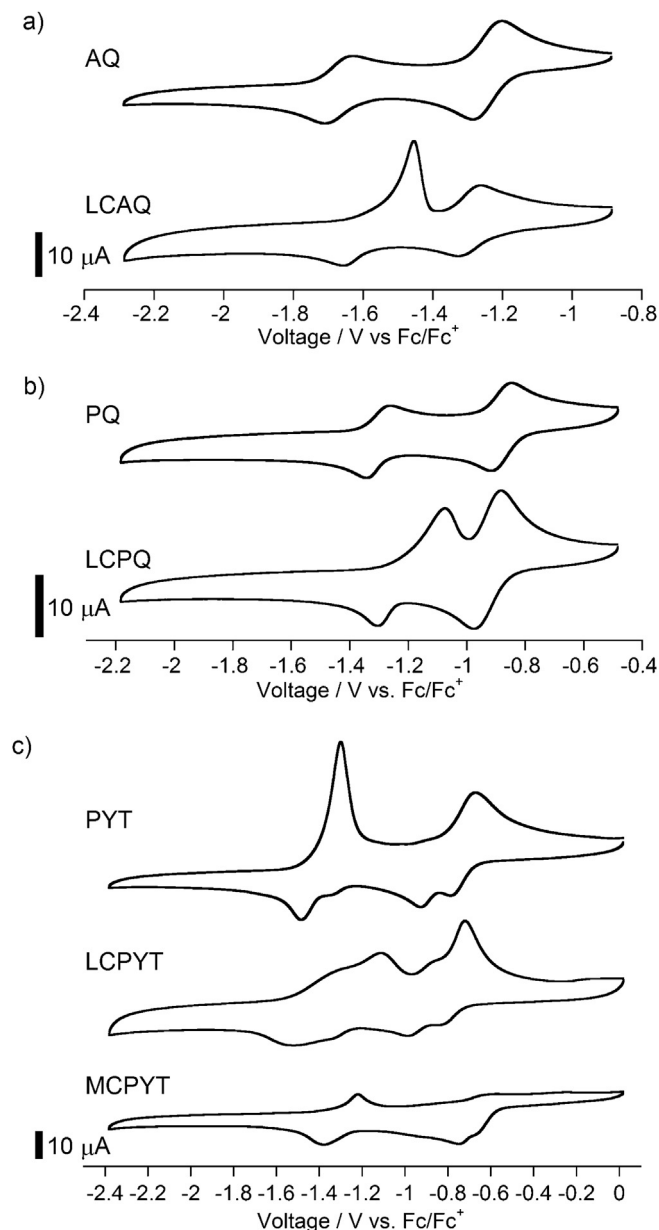
## 3. Results and discussion

### 3.1. Redox property of LC-quinones

Redox property of LC-quinones was studied by cyclic voltammetry (CV) in 0.1 M LiBF<sub>4</sub>/DMSO (Fig. 2). Some compounds exhibited complex-shaped voltammograms, although the reason is not clear at present. We therefore discuss the redox properties of LC-quinones using reduction peak potentials. LCAQ gave two redox



Scheme 1. Synthesis of a) LCAQ, and b) LCPQ, LCPYT, and MCPYT.



**Fig. 2.** Cyclic voltammograms of quinones. a) AQ and LCAQ, b) PQ and LCPQ, and c) PYT, LCPYT, and MCPYT. Conditions; sample concentration: 1 mM (0.5 mM for LCAQ and LCPYT), supporting electrolyte: 0.1 M LiBF<sub>4</sub>, solvent: DMSO, working electrode: glassy carbon, counter electrode: Pt, reference electrode: Ag/AgNO<sub>3</sub>, scan rate: 0.1 V s<sup>-1</sup>, temperature: rt. Potentials were corrected using ferrocene (Fc/Fc<sup>+</sup>) as an internal standard. The currents for LCAQ and LCPYT were doubled.

waves, corresponding to the reduction to the corresponding dianion species. The first reduction peak potential for LCAQ is slightly lower than that for AQ, but the second reduction peak potential for LCAQ is slightly higher than that for AQ (Fig. 2a). As a result, average reduction peak potential for LCAQ is similar to that for AQ. This is also the case for *o*-quinones, PQ and PYT. LCPQ gave two one-electron redox waves corresponding to the reduction to the corresponding dianion species (Fig. 2b). The average reduction peak potential for LCPQ is similar to that for PQ. LCPYT gave two two-electron redox waves corresponding to the reduction to the corresponding tetraanion species. The average reduction peak potential is similar to that for PYT (Fig. 2c). These results of CV studies indicate that introduction of two -CO<sub>2</sub>Li groups causes very small

change of the reduction peak potentials of *p*- and *o*-quinones, AQ, PQ, and PYT.

### 3.2. Theoretical calculations

To get deeper understanding of the redox behavior of LC-quinones, we carried out theoretical calculations (Table 1, Table S1, and Fig. S2 in Supporting Information). LUMO energy levels of LCAQ, LCPQ, and LCPYT and LUMO + 1 energy level of LCPYT are slightly higher than those of the corresponding parent quinones. However, the differences are not very large, which is consistent to the CV results. We also calculated the total energy changes for reduction process. We divided the reduction process in the presence of Li ions into two processes; the reduction of quinones and the coordination of the reduced quinones to Li ions (Fig. S2). The energies for reduction ( $E_{\text{red},n}$ , in which  $n$  indicates the first, second, third, or fourth redox processes) and coordination ( $E_{\text{coord},n}$ ) are shown in Table 1. It is interesting that  $E_{\text{red}}$ ,  $E_{\text{coord}}$ , and  $E_{\text{total}}$  values of LC-quinones are very similar to those of the corresponding parent quinones. Therefore the potentials of the batteries can also be predicted by the energy difference between the charged- and discharged-states which include coordination to Li ions [39,55].

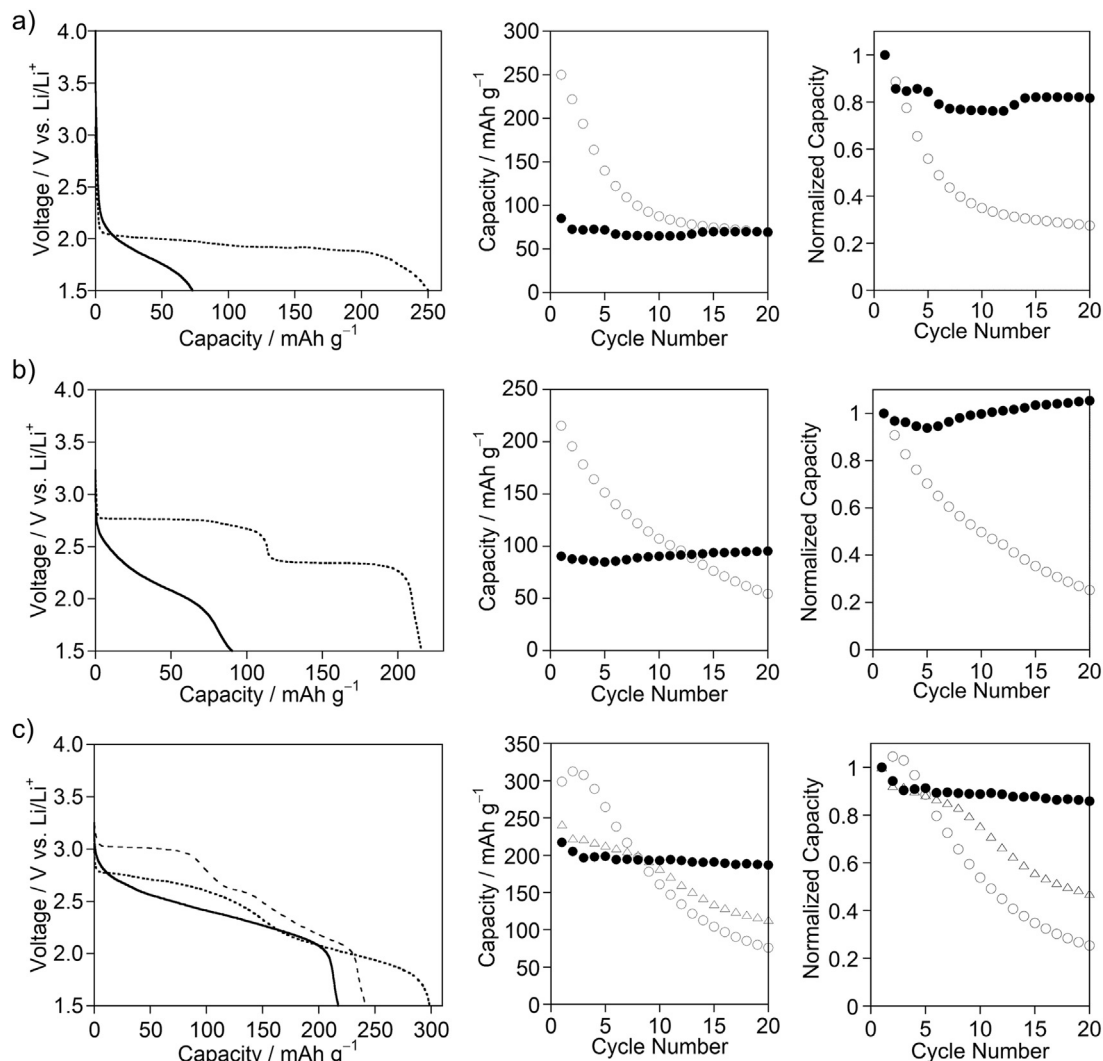
### 3.3. Battery performance of LC-quinones as cathode materials

To examine the effect of -CO<sub>2</sub>Li groups to the cyclability of the batteries, we measured the performances of the batteries using LC-quinones as cathode materials. At first, performance of the battery using LCAQ was studied (Fig. 3a). The initial capacity is 85 mAh g<sup>-1</sup>, which is 49% of the theoretical capacity. Reduction of two -CO<sub>2</sub>Li groups are not involved in the discharge process because the cutoff voltage of 1.5 V vs. Li/Li<sup>+</sup> is much higher than the discharge voltage of dilithium terephthalate (0.8 V vs. Li/Li<sup>+</sup>) [44]. The effect of the -CO<sub>2</sub>Li groups on the redox potential is not significant. Mean discharge voltages of the battery using LCAQ (1.79 V vs. Li/Li<sup>+</sup>) is only slightly lower than that of AQ (1.92 V vs. Li/Li<sup>+</sup>). The battery using LCAQ exhibited good cyclability. Capacity does not decrease significantly for 20 cycles. After 20 cycles, discharge capacity is 70 mAh g<sup>-1</sup>, which is 82% of the initial capacity, while that of the battery using AQ is 69 mAh g<sup>-1</sup>, which is 28% of the initial capacity.

**Table 1**

Theoretically calculated energies of unoccupied MOs and redox processes for AQ, LCAQ, PQ, LCPQ, PYT, LCPYT, and MCPYT.

	LUMO/eV (LUMO + 1/eV)	<i>n</i>	$E_{\text{red},n}$ /eV	$E_{\text{coord},n}$ /eV	$E_{\text{total},n}$ /eV
AQ	-2.79	1	-4.27	6.12	1.85
		2	-4.58	6.71	2.13
LCAQ	-2.64	1	-4.25	6.26	2.01
		2	-4.65	6.87	2.22
PQ	-2.98	1	-4.12	7.72	3.60
		2	-4.38	6.75	2.37
LCPQ	-2.77	1	-4.17	7.75	3.58
		2	-4.39	6.75	2.36
PYT	-3.56 (-3.46)	1	-3.44	7.15	3.71
		2	-3.80	7.37	3.58
		3	-4.18	6.56	2.38
		4	-4.60	6.92	2.31
LCPYT	-3.33 (-3.12)	1	-3.55	7.23	3.68
		2	-3.87	7.44	3.57
		3	-4.23	6.60	2.37
		4	-4.64	6.94	2.30
MCPYT	-3.91 (-3.73)	1	-3.05	6.84	3.78
		2	-3.41	7.07	3.66
		3	-3.79	6.21	2.42
		4	-4.20	6.56	2.35



**Fig. 3.** Charge–discharge curve and cycling (0.2 C rate) of a) AQ (dotted line, open circle) and LCAQ (solid line, filled circle), b) PQ (dotted line, open circle) and LCPQ (solid line, filled circle), and c) PYT (dotted line, open circle), LCPYT (solid line, filled circle), and MCPYT (dashed line, open triangle) in LiPF<sub>6</sub>/PC.

Next, performance of the battery using LCPQ was studied (Fig. 3b). The initial capacity is 90 mAh g<sup>-1</sup>, which is 52% of the theoretical capacity. Mean discharge voltage (2.11 V vs. Li/Li<sup>+</sup>) is lower than that of the batteries using PQ (2.53 V vs. Li/Li<sup>+</sup>), although the reason is not clear at present (Fig. 3b). High cyclability is also remarkable. After 20 cycles, discharge capacity of the battery using LCPQ is 95 mAh g<sup>-1</sup>, which is 105% of the initial capacity, while that of the battery using PQ is 54 mAh g<sup>-1</sup>, which is 25% of the initial capacity.

Finally, performance of the battery using LCPYT was studied (Fig. 3c). The initial capacity is 217 mAh g<sup>-1</sup>, which is 73% of the theoretical capacity. Mean discharge voltage (2.39 V vs. Li/Li<sup>+</sup>) is slightly higher than that of the batteries using PYT (2.32 V vs. Li/Li<sup>+</sup>). After 20 cycles, discharge capacity of the battery using LCPYT is 187 mAh g<sup>-1</sup>, which is 86% of the initial capacity, while that of the battery using PYT is 76 mAh g<sup>-1</sup>, which is 25% of the initial capacity.

These results indicate that two –CO<sub>2</sub>Li groups decrease the solubility of the LC-quinones in electrolyte solutions. However, it is uncertain whether the lithium atom of –CO<sub>2</sub>Li group plays an important role in decreasing the solubility. To verify the importance of the –CO<sub>2</sub>Li groups for cyclability, we studied MCPYT, which has –CO<sub>2</sub>Me groups instead of –CO<sub>2</sub>Li groups and cannot form a

network by coordination to Li ions. MCPYT exhibited redox waves with slightly higher potentials than LCPYT in CV, which is consistent to the theoretical calculations (Fig. 2, Table 1). The battery using the MCPYT exhibited slightly higher mean discharge voltage of 2.61 V and the initial capacity of 242 mAh g<sup>-1</sup> in LiPF<sub>6</sub>/PC (Fig. 3c). However, the battery exhibited poor cyclability; the capacity at 20 cycles is 47% of the initial capacity. The result strongly indicates that the lithium atom of –CO<sub>2</sub>Li group decreases the solubility of the LC-quinones in electrolyte solutions presumably *via* formation of a network by Li-coordination. In addition, the utilization ratios of LCAQ and LCPQ are lower than those of parent quinones. Presumably, the network by Li-coordination, which makes LC-quinones behave as polymers, reduces the utilization ratios. A network similar to that observed in the crystal of dilithium terephthalate [42] seems to be plausible, although the detail is not clear at present.

Lithium batteries using LCAQ, LCPQ, and LCPYT also exhibited good cyclability in an equimolar complex LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>/tetraglyme (LiTFSAG4) which behaves as a room-temperature ionic liquid [56]. Discharge capacities of the batteries using LCAQ, LCPQ, and LCPYT are 73, 96, and 85% of the initial capacity after 20 cycles, respectively (Fig. S4 in Supporting Information).



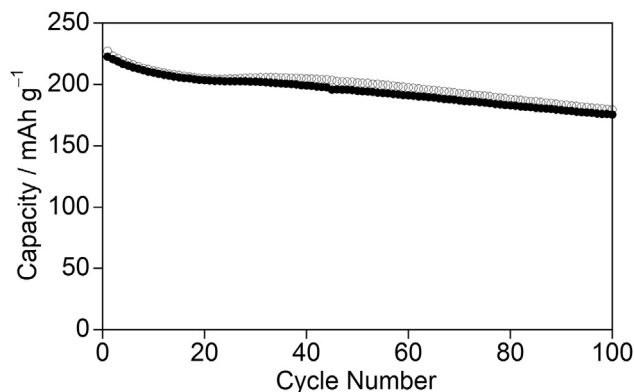


Fig. 4. Charge–discharge cycling of LCPYT in LiTfSA/G4 at 45 °C. Charge (filled circle) and discharge (open circle).

#### 3.4. Cyclability and rate performance of LCPYT as a cathode material

The battery performance of LCPYT was studied in more details, because it showed the highest capacity. The battery exhibited initial capacity of 257 mAh g<sup>-1</sup>, which is 87% of the theoretical capacity, and mean discharge voltage of 2.39 V vs. Li/Li<sup>+</sup>. Therefore, the energy density is calculated to be 614 mWh g<sup>-1</sup>, which is comparable to that of LiCoO<sub>2</sub>. Cyclability is good. The discharge capacity after 100 cycles is 78% of the initial capacity (Fig. 4). In addition, the battery exhibited fast charge ability. The cell was charged at various rates with a constant discharge rate of 59 mA g<sup>-1</sup> (0.2 C rate)

(Fig. 5a). The charge capacity of the battery at 148, 295, 591, and 1479 mA g<sup>-1</sup> is 94, 91, 86, and 75% of that at 59 mA g<sup>-1</sup>, respectively. However, the discharge cannot be so fast. The discharge capacity at 148, 295, 591, and 1479 mA g<sup>-1</sup> is 96, 69, 38, and 16% of that at 59 mA g<sup>-1</sup>, respectively (Fig. 5b). Removal of Li ions from the cathode seems to be easier than insertion because of strong coordination of tetraglyme to Li ions.

#### 4. Conclusion

Introduction of two –CO<sub>2</sub>Li groups to quinones serves as a simple and effective approach to decrease the solubility of various quinones in electrolyte solutions without significant decrease in the voltage. Batteries using quinones having –CO<sub>2</sub>Li groups as a cathode material exhibited excellent cyclability compared to those using the parent quinones. In particular, the battery using LCPYT exhibited high energy density, high cyclability, and fast charge ability. This simple approach should be applicable to other organic cathode materials of low molecular weight, which suffer from high solubility in electrolyte solutions. This finding opens a new way of improving the performance of Li-ion batteries using organic cathode materials.

#### Acknowledgments

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.03.027>.

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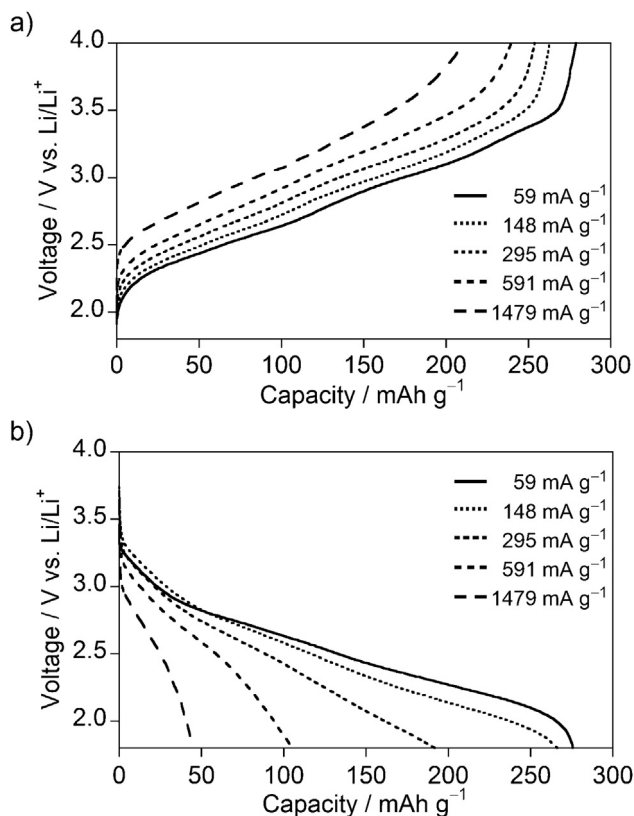


Fig. 5. Charge and discharge curves of LCPYT/Li battery in LiTfSA/G4 at 45 °C at various rates. a) Charge rate ability (59, 148, 295, 591, and 1479 mA g<sup>-1</sup>) and b) discharge rate ability (59, 148, 295, 591, and 1479 mA g<sup>-1</sup>).

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